

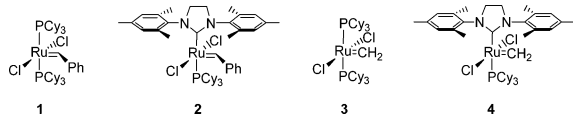
DFT Prediction and Experimental Observation of Substrate-Induced Catalyst Decomposition in Ruthenium-Catalyzed Olefin Metathesis

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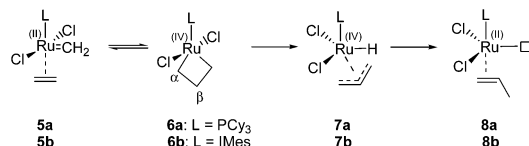
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The development of ruthenium carbene complexes such as **1** and **2** has transformed olefin metathesis into a versatile tool in organic and polymer chemistry.¹ Unraveling the fundamentals of metathesis catalyst decomposition is of critical importance, because the control of decomposition pathways would result in increased catalyst efficiency. Despite this, relatively few reported experimental studies focus on decomposition.² Grubbs and co-workers³ have investigated the thermal decomposition of first- and second-generation methylenecarbene complexes **3** and **4**, which are thermally the most unstable intermediates in the metathesis catalytic cycle. To the best of our knowledge, no theoretical studies dedicated to resolving the cause and/or prevention of ruthenium metathesis catalyst decomposition have been published.⁴



In the current study, a substrate-induced decomposition route, involving β -hydride transfer from a ruthenacyclobutane intermediate (Scheme 1), is proposed, investigated by density functional theory (DFT) methods,⁵ and confirmed experimentally.

Scheme 1



Ruthenacyclobutanes **6** are low-energy intermediates in the active olefin metathesis mechanism as supported by a number of theoretical mechanistic studies.⁶ In principle, the formation of a Ru^{IV} allyl-hydride species **7** from the ruthenacyclobutane **6** could compete with the conventional metathesis sequence (**5** \leftrightarrow **6**). Subsequent reductive elimination would induce transfer of the hydride in **7** to the terminal position of the allylic fragment resulting in the formation of a coordinatively unsaturated Ru complex **8**, which should be inactive for metathesis. The relevance of this proposed decomposition route is supported by related transformations observed for substituted ruthenacyclobutanes,⁷ Ru-allyl formation by β -hydrogen abstraction from ruthenacyclobutanes,⁸ a theoretical study on β -hydrogen elimination of ruthenacyclopentanes,⁹ and a recent DFT study on β -hydride transfer in a related ruthenacyclobutane complex.¹⁰

The DFT-calculated Gibbs free energy (ΔG at 298.15 K) surface for conversion of **6** to **8** for both first- (L = PCy₃) and second-

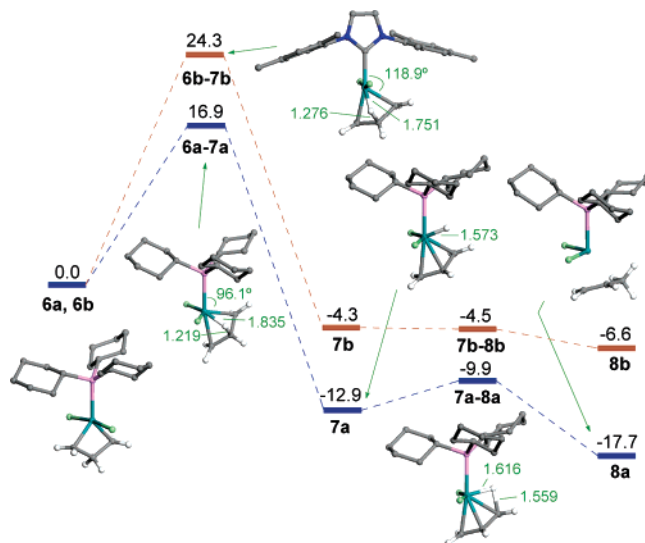


Figure 1. Selected geometries and relative calculated ΔG_{298} energies (kcal/mol) for stationary points on the potential energy surface for decomposition of ruthenacyclobutanes **6a** and **6b** (hydrogen atoms on the ligands are omitted for clarity).

generation (L = IMes) ligand systems is shown in Figure 1. β -Hydride transfer from **6a** is calculated to proceed with an activation barrier (ΔG_{298}^\ddagger) of 16.9 kcal/mol compared to an activation barrier of 24.3 kcal/mol from **6b**. An earlier transition state for **6a**–**7a** is suggested by the relatively elongated Ru–H distance for **6a**–**7a** (1.835 Å) compared to the Ru–H distance in **6b**–**7b** (1.751 Å). The higher relative energy of **6b**–**7b** may be ascribed to greater steric interaction of the heterocyclic ligand with the ruthenacyclobutane fragment, resulting in the larger C_{NHC}–Ru–C angle (118.9°) for **6b**–**7b** compared to the corresponding P–Ru–C angle (96.1°) for **6a**–**7a** (Figure 1). Propene formation, via hydride transfer back to a terminal allyl carbon in **7a** and **7b**, is calculated to be facile for the first-generation catalyst ($\Delta G_{298}^\ddagger = 3.0$ kcal/mol; $\Delta G_{298} = -4.8$ kcal/mol) and proceeds essentially without barrier¹¹ for the second-generation catalyst ($\Delta G_{298} = -2.3$ kcal/mol).

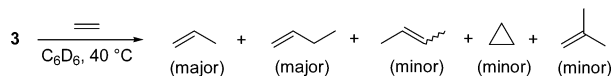
The calculated barriers for β -hydride transfer are not excessively higher than the expected barriers for metathesis from **6**,¹² strengthening the feasibility of the decomposition route. The calculated barriers for decomposition suggest that the first-generation catalyst should be more amenable for the proposed decomposition route compared to the second-generation catalyst. Irreversible loss of the metathesis active complexes **5** and **6** is dictated by the exothermic nature of allyl-hydride **7** formation and facile formation of metathesis inactive complexes **8**. These 14-electron complexes, containing two open coordination sites on Ru, could essentially follow a number of subsequent decomposition pathways.

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In an effort to confirm these theoretical findings experimentally, the degenerate Ru-methylidene-catalyzed metathesis of ethylene was performed. This approach eliminated the possibility of higher olefin formation from metathesis and provided the opportunity to detect olefin formation via alternative mechanisms. Thus, a saturated ethylene solution containing complex **3** in benzene-*d*₆ was heated at 40 °C for 16 h. After such time, ¹H NMR and GC analysis revealed the formation of propene, 1- and 2-butenes, as well as small amounts of cyclopropane and isobutene (Scheme 2).^{13,14}

Scheme 2



The formation of propene is rationalized by the β -hydride transfer mechanism (Scheme 1) and 1-butene, 2-butene, and isobutene can be obtained when propene is used as a substrate by β -hydride transfer of either α -methylruthenacyclobutane (yielding 1-butene or 2-butene) or β -methylruthenacyclobutane (yielding isobutene).^{7b} Alternatively, the formation of 2-butene by self-metathesis of propene or from isomerization^{2c} of 1-butene (e.g., by reversible allyl-hydride formation) cannot be excluded. Possible reductive elimination of cyclopropane⁴ from ruthenacyclobutane **6a** emphasizes the argument that ruthenacyclobutanes act as decomposition precursors during substrate-induced decomposition of **3**. Preliminary DFT calculations indicate that reductive elimination of cyclopropane from **6** is less facile than β -hydride transfer, in agreement with the experimentally observed decomposition product distributions, while alternative α -hydride transfer in **6** is unlikely to account for propene or 1-butene formation.¹⁵

In a similar experiment (excess ethylene, 16 h, 40 °C) with the second-generation methylidene **4**, it was found that 38% of the starting methylidene had decomposed. ¹H NMR and GC analysis revealed the formation of predominantly propene, as well as 1- and 2-butene and trace amounts of isobutene and 1,3-butadiene.^{14,16} In addition, the imidazolium salt, [H₂IMesH]Cl,¹⁷ was identified as a primary decomposition species.¹⁸ In contrast to the results obtained for decomposition of **3**, the yield of propene was surprisingly found to be ca. 1.5 times in excess relative to the amount of decomposed **4**. This shows that the propene yield from decomposition of **4** cannot directly be correlated to methylidene loss. This intriguing result either suggests the catalytic formation of propene via an alternative mechanism to β -hydride transfer or that a Ru-methylidene species is regenerated after a β -hydride transfer/propene formation step. Both the different product distributions during degenerate ethylene metathesis with **3** and **4**, as well as the relatively unfavorable β -hydride transfer barrier calculated for **4**, do, however, suggest that an alternative propene-yielding mechanism may also be operating for the second-generation catalyst.

In conclusion, theoretical and experimental evidence support substrate-induced decomposition of Ru-carbene olefin metathesis catalysts, albeit that the proposed mechanism was not shown to be obligatory. The results provide significant new insight into the nature of Ru-carbene catalyst decomposition under catalytic conditions. Further investigations on the role of substrate during catalyst decomposition are in progress.

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Supporting Information Available: Detailed theoretical methods, Cartesian coordinates of optimized structures, and experimental data and procedures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) Calculated electronic energy barrier (ΔE^\ddagger , 0 K) for **7b** \rightarrow **8b** is 0.8 kcal/mol, but upon addition of thermodynamic corrections at 298.15 K, a negative ΔG^\ddagger_{298} barrier of -0.2 kcal/mol is found, effectively suggesting barrierless transformation of **7b** to **8b**.
- (12) Activation barriers for metathesis to proceed from the ruthenacyclobutane intermediates are estimated to be 9.6 and 12.0 kcal/mol for corresponding first- and second-generation models in a recent DFT/BP86 theoretical study by Adlhart and Chen.^{6a}
- (13) ¹H NMR analysis after 16 h showed complete disappearance of the methylidene peak of **3** and an α -olefin yield of 20%. GC-determined product ratios: propene/1-butene/2-butene/cyclopropane/isobutene = 60:21:10:7:2.
- (14) Additional PCy₃ decomposition complexes are formed. One- and two-dimensional ¹H and ³¹P NMR analyses revealed a concentration dependence of these species with ethylene concentration; see Supporting Information.
- (15) See Supporting Information.
- (16) Relative ratios of observed olefins (GC): propene/1-butene/2-butene = 87/4/9. The dinuclear ruthenium complex isolated from the thermal decomposition of **4** by Grubbs et al.^{3b} was not observed from the ¹H NMR analysis.
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- (18) Isolated in 13% yield as a colorless solid. For additional ²H labeling studies on the role of [H₂IMesH]Cl during decomposition, with and without the presence of substrate, see Supporting Information.

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